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CHARACTERIZATION OF CHEMICALS ON ENGINE EXHAUST PARTICLES: F101 AND F110 ENGINES

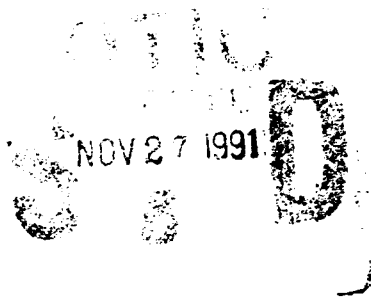
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<p>Assesment of the environmental impact of aircraft operations is required by Air Force regulations. This program was undertaken to quantify chemicals associated with particulate emissions of two Air Force turbine engines (F101 and F110). The emissions tests were carried out using a test cell at Tinker AFB OK. Emissions were sampled at four power settings for each engine. Measurements were made of particle mass concentration, elemental (inorganic) components, and of target PAH and NO₂-PAH vapor and particulate components. A sampling device was designed and constructed for use on top of the test cell exhaust stack. Analyses of samples collected were performed using analytical balances for mass determinations, Spark Source Mass Spectroscopy for elemental determinations, gas chromatography-mass spectroscopy for analyses of PAH, and Scanning Electron Microscopy for examination of particle morphology. Results obtained indicate that these two engines have much lower emission concentrations of particles and organics than any engines we have previously tested. The emissions of target PAH compounds found to be lowest for these engines at full (nonafterburning) power, while the particulate emissions are highest at this power.</p>													
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PREFACE

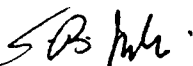
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This final report describes the experimental methods and presents the results and analysis of the selected gas and particle components of exhaust from two gas turbine engines. This work was performed between June 1988 and March 1989. The AFESC project officer was Mr Surendra Joshi.

Principal Battelle staff involved in performance of this work were Mr W.C. Baytos, Ms J.C. Chuang, and Dr M.R. Kuhlman. Engine testing at Tinker AFB was conducted with the cooperation and assistance of the Production Engine Test Section; we are especially grateful for the assistance provided by Mr David Hughes.


This report has been reviewed by the Public Affairs Officer (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.


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SECTION I

INTRODUCTION

A. OBJECTIVE

The Air Force Engineering and Services Center (AFESC) is working on a joint program with the Naval Air Propulsion Center to update an engine emission catalogue, last updated in 1978. This joint program was established to review all available emission data on military gas turbine engines, assess the validity of these data for current engine models, identify deficiencies in the data, and develop an engine emission data base. One deficiency was the paucity of data on particulate-bound chemicals emitted from military aircraft. The work described in this report is one portion of a study conducted for AFESC to characterize chemicals on engine exhaust particles and determine their occupational and environmental significance.

B. BACKGROUND

Exhaust particles are responsible for much of the visible emissions from jet engines and consist of a complex collection of aerosols that varies qualitatively and quantitatively as a function of engine type, fuel composition, and operating mode. A large percentage of the aerosol material is unburned carbon of submicron size. This material is non-reflective, nonpolar, and relatively stable, chemically and physically.

A more reactive component of the exhaust particulate matter is the material consisting of condensed hydrocarbons and/or hydrocarbons sorbed on the carbon particles. This segment of the aerosol is a complex mixture of unburned, partially oxidized and reformed hydrocarbons with varying vapor pressures, chemical reactivities, physical and optical properties.

The particulate-bound organics form a very small fraction of the total organic composition of the jet exhaust from a mass balance standpoint. However, these particulate-bound chemicals, along with the aerosol components which contain certain trace elements (e.g., heavy metals), may be occupationally and environmentally significant because of the small size of the typical exhaust particles. These small particles can be

entrained in the innermost parts of the human respiratory tract. Thus, the toxic and mutagenically active chemicals bound to the surfaces of these invading particles may be biologically activated within the body and human illness may result.

C. SCOPE

The work described in this report consists primarily of collection and chemical analysis of particulate and vapor portions of the exhaust from the F101 and F110 engines operated at specified power levels. Measurement of the target polycyclic aromatic hydrocarbons (PAH) and nitro-PAH concentration in the constitutes a major portion of the efforts expended. The work reported here was performed in conjunction with another task, separately reported⁽¹⁾, which was concerned with the measurement of gaseous emissions from the engines and the measurement of the physical parameters of the emitted aerosol particles.

SECTION II

EXPERIMENTAL METHODS

A. ENGINES AND ENGINE TEST FACILITY

The engines included in this study were operated in two indoor test cells at Tinker Air Force Base, Oklahoma. The F110 engine (S/N509153), which powers some models of the F-16 fighter was operated in Test Cell 11, and the F101 engine (S/N470135), two of which provide the F111's power plant, was operated in Test Cell 12. Both engines are General Electric designs, and had not logged operational hours before testing. The engine exhaust flows into a 4.85-meters diameter cone and through a 26-meters long steel augmentor tube, the last 9 meters of which are perforated with numerous 3.2-cm holes. This perforated portion is housed in a blast room, vented to the atmosphere by means of fifty-six 0.9-meter diameter vertical vents, as indicated in the test cell cross section shown in Figure 1.

The engine test cell is equipped to monitor all important parameters relevant to engine operation on a continuous basis. These parameters include air temperatures and pressures, fuel flow, air flow, thrust, fan speed, core speed, turbine blade temperatures, and other derived measures. Figure 1 indicates the position of the sampling rake used in the companion study⁽¹⁾, and the sampling position used atop the exhaust stack for this study.

B. EXHAUST SAMPLING

Exhaust samples were collected at each of four predetermined engine operating power levels, ranging from idle to intermediate (~100 percent of rated thrust in nonafterburning mode). Sampling was initiated after the engine operating parameters had stabilized at the desired power, and was concurrent with the sampling performed in the companion project.

The samples collected at each operating power included particulate matter on three different media and vapor phase organic compounds on XAD-2 resin. Particulate samples were collected on Millipore® type AA 47-mm filters for subsequent elemental analysis and on Nuclepore® 0.1 μm pore

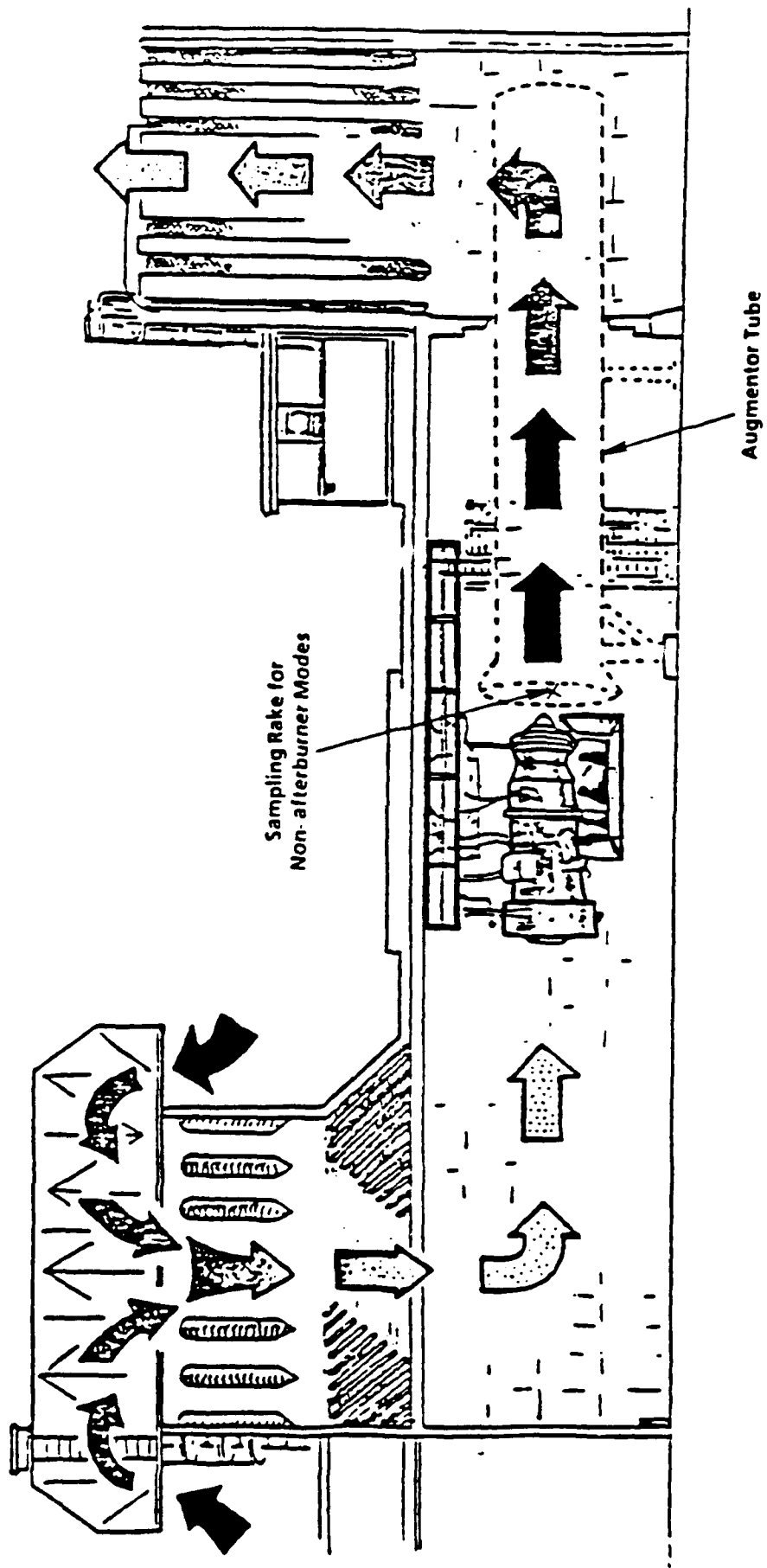


Figure 1. Test Cell Cross Section

47-mm filters for examination by scanning electron microscopy (SEM). Pallflex® QAST quartz fiber 20 by 25 cm filters were also used for collection of particulate samples for subsequent extraction and analysis for target PAH compounds.

A sampling apparatus was designed to permit collection of all required samples and ancillary information from the top of the exhaust stack of the engine test cells. Two such sampling outfits were constructed to minimize delays between sampling at successive engine power levels. The main elements of the sampling apparatus are depicted in Figure 2. The design permitted monitoring the flow rates and gas temperatures and controlling the sampling flow rates from a lower level of the test cell roof. Lines leading to the sampling gear were secured to spaces between the exhaust cell stacks and insulated to prevent damage from the hot exhaust gases. During sampling, the various flow rates and temperatures were recorded on data forms by the sampling team. After sampling was completed at a given power setting, the engine was turned off and the sampling gear retrieved as soon as the temperature on top of the stack permitted safe access. The large filter's face was covered, and all the collected samples were lowered from the top of the exhaust stack in their holders. These samples were removed to an inside location and placed in transport containers and the filter holders and sorbent cartridge holder were reloaded while the duplicate sampling rig was being installed on the exhaust stack by other members of the sampling team.

In addition to providing for sample flow rate measurement by means of orifices attached to the two high flow rate blowers, and by rotameters connected to the 47-mm filter holders, the sampling apparatus included thermocouples for measurement of the gas temperature at the inlet to the high-volume filter and at the outlet from the sorbent cartridge, and a pitot tube for measurement of the gas flow rate through the exhaust stack. This apparatus was assembled and tested under anticipated operating temperatures before it left the Columbus, Ohio, laboratories.

Several steps were necessary for the preparation of the sampling media used in the emissions sampling. The sorbent traps were precleaned and dried, following the usual procedure, and stored in light-tight, sealed,

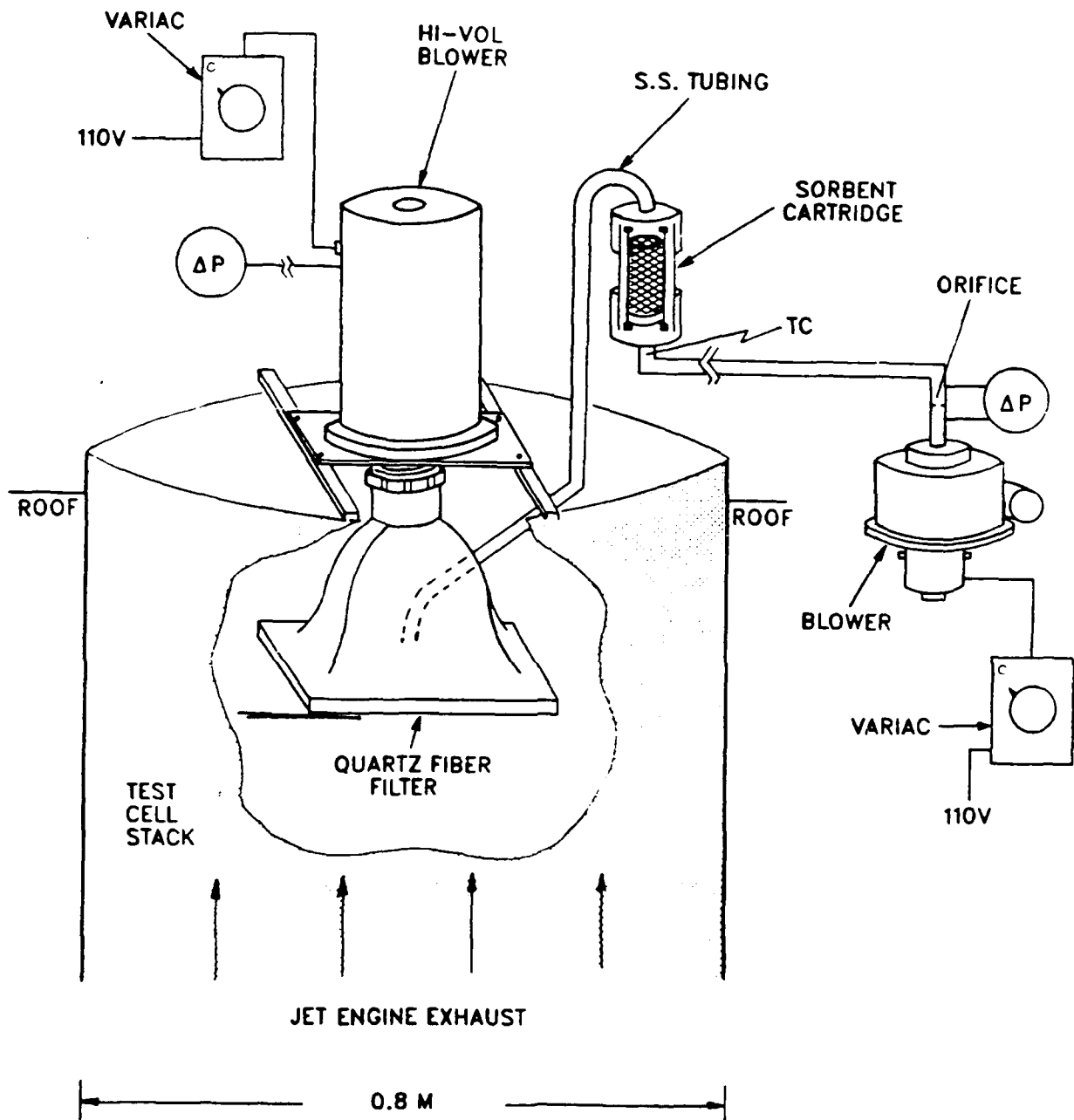


Figure 2. Schematic of Principal Components of Sampling System
(Not Shown are Pitot Tube and 47-mm Filter Holders)

labeled jars for transport to the field. The quartz fiber filters used in emissions sampling were prepared by heating in a muffle furnace at 450°C for at least 16 hours prior to being placed in sealed containers for transport to the field. Tare weights were determined for the quartz fiber high-volume and Millipore® filters, according to standard procedures. The tared filter media were stored in labeled containers prior to their removal from the balance room. The high-volume filters were enclosed in aluminum foil which had been muffled, and inserted in labeled manila folders, sealed in polyethylene zip-lock bags for transport. The Millipore® filters were placed in labeled petri slides for transport. To serve as controls on the gravimetric determinations, several filters of each type remained in the weighing laboratory, and others were taken to the field but not used for sample collection.

C. ANALYSIS OF SAMPLES

1. Inorganic Analysis

Inorganic analysis consisted of Spark Source Mass Spectroscopy (SSMS) analysis of the particulate matter collected on Millipore® filter media. The analytical technique, SSMS, was selected because of its superior sensitivity and its ability to detect all trace elements of concern.

As performed at Battelle, SSMS is used to provide data for all elements except H, C, N, O, inert gases, and elements with no stable isotope. To obtain high sensitivity, the inorganic contaminants are separated from the carbonaceous and organic material present in the particulate and filter. An oxygen plasma asher is used to remove the unwanted organic fraction of the sample. The remaining inorganic material is then mixed with high-purity graphite for the analysis. This level of sensitivity should permit detection of 0.01 µg of the elements of interest. The accuracy expected of the SSMS analysis is ± a factor of three with a precision of ± a factor of two.

2. Organic Analysis

a. Extraction Method

The filter and XAD-2 samples obtained from each test were extracted separately with methylene chloride (distilled-in-glass) by Soxhlet® extraction for at least 16 hours or until the solvents in the top extraction chamber were clear. In previous studies^(2,3) we have demonstrated that by using this extraction technique, the extraction efficiencies for most PAH, mono-nitro PAH, and dinitro-PAH from diesel exhaust particulate matter are usually greater than 80 percent. The extracts were each concentrated to 2 mL by Kuderna-Danish (K-D) evaporation. Aliquots of each extract were used to determine the residue weights.

One-half of each extract was analyzed by electron impact (EI) gas chromatography/mass spectroscopy (GC/MS) for PAH compounds and by negative chemical ionization (NCI) GC/MS for determination of nitro-PAH and oxygenated PAH. The other half of the extract have been stored for possible future use in bioassay studies.

b. Selection of Target Compounds

In general, the selection of target compounds to be studied on the jet exhaust particles is mainly based on: (1) the mutagenicity and/or carcinogenicity of the compounds, (2) identification of compounds from the exhaust particles from related studies, and (3) the availability of analytical standards. The selected target compounds are summarized in Table 1.

c. Gas Chromatography/Mass Spectrometry (GC/MS) Method

A Finnigan Model 4500 GC/MS equipped with a Carlo Erba on-column injector was used for the GC/MS analyses. An Ultra® 2 cross-linked 5 percent phenyl methyl silicone fused silica capillary column was used as both the GC column and the transfer line between the GC oven and the MS ionization source. Data collection and processing were performed by a Finnigan INCOS Model 2300 data system. Typical GC/MS operating conditions are given in Table 2.

TABLE 1. TARGET COMPOUNDS FOR GC/MS ANALYSES

COMPOUND	EVIDENCE OF CARCINOGENICITY	REMARKS
Naphthalene		
Acenaphthalene		
Dibenzothiophene		
Phenanthrene	No	Not active; marker for volatile PAH
Anthracene	No	Not active; marker for volatile PAH
Fluoranthene	No	Not active; marker for total PAH; nitro-derivatives are mutagens
Pyrene	No	Nitro-derivatives are mutagens
Benz[a]anthracene	Yes	Also is precursor for DMBA, a potent carcinogen
Chrysene	Limited	Weak mutagen; some methyl derivatives are very active
Cyclopenta[c,d]pyrene	Limited	Active mutagen
Benzofluoranthenes	Yes	Active mutagens and carcinogens
Benzo[e]pyrene	Inadequate	Limited activity
Benzo[a]pyrene	Yes	Active mutagen and carcinogen
Indeno[1,2,3,-c,d]pyrene	Yes	Has been identified in mobile sources
Benzo[g,h,i]perylene	Inadequate	Weak carcinogen
Dibenzo[a,h]anthracene	Yes	

TABLE 1. TARGET COMPOUNDS FOR GC/MS ANALYSES (CONCLUDED)

COMPOUND	EVIDENCE OF CARCINOGENICITY	REMARKS
2-Nitro-1-naphthol		
4-Hydroxy-3-nitro- biphenyl		
1-Nitronaphthalene		
2-Nitronaphthalene		
9-Nitroanthracene		
9-Nitrophenanthrene		
Nitroanthracene/ phenanthrene		
3-Nitrofluoranthene	Mutagen	
1-Nitropyrene	Mutagen	
6-Nitrochrysene		
Dinitropyrene isomer	Mutagen	

TABLE 2. GC/MS OPERATING CONDITIONS

GC PARAMETERS

Column	Ultra No. 2 fused silica, cross-linked 5% phenyl methylsilicone, 50 m x 0.31 mm I.D., 0.52 μ m film (Hewlett-Packard)
Carrier	CH ₄ , velocity 50 cm/sec at 250°C
Sample Injection	1-2 μ L, on-column mode or splitless mode
Program	45 C; 1 min; ballistically to 150°C, 3 min; 150°C to 320°C at 6°C/min; hold for 20 min

MS PARAMETERS

Interface	320°C; fused silica column directly introduced into ion source
Typical Full Mass Scan Range	45 to 450 amu at 1 sec/scan in EI mode 100 to 450 amu at 1 sec/scan in NCI mode
Multiple Ion Detection	Selected target molecular ion monitored
Filament Emission Current	0.3 ma
Signal Amplifications	10 ⁻⁷ amp/volt with 10 ⁵ electron multiplier gain
Electron Energy	70 eV
NCI Reagent Gas	CH ₄ at ~1.0 torr; 150 eV
Ionizer Temperature	180°C

Before analysis of standards or samples, the system is calibrated by introducing a standard substance, perfluorotributylamine (FC-43) and determining the mass assignment for principal fragment ions. The mass calibration table is stored and used to calibrate the ion masses over the scanning range. A quantitative multiple-ion detection (MID) GC/MS analysis is also carried out for the samples. Typically, the sensitivity for the analysis of PAH increases approximately 100 times in the MID mode as compared to the full scan mode. A three-point standard curve is generated for each of the target compounds. The standards are analyzed in triplicate, along with a blank sample to determine the baseline. The internal standard, 9-phenyl-anthracene, will be added to the standards and the samples at a fixed concentration level. The response factor for each compound will be generated from the calibration curve. The identification of the target compounds in the extracts is based on the correct molecular ion and the correct retention time relative to the internal standard, as determined from the standard analyses. The quantification of each target compound is based on the following equation:

$$C_s = \frac{A_s \cdot C_{is}}{A_{is} \cdot R_f}$$

where

- C_s = Concentration of a target compound, ng/ μ L
- A_s = Molecular ion area of a target compound
- C_{is} = Concentration of the internal standard, ng/ μ L
- A_{is} = Molecular ion area of the internal standard
- R_f = Response factor of a target compound.
- d. Negative Chemical Ionization, Gas Chromatography/Mass Spectrometry (NCI GC/MS)

The NCI on-column injection GC/MS method provides significant benefits for the analysis of nitro-aromatic compounds over the conventional EI GC/MS method. The on-column injection at a lower temperature avoids degradation of the thermally labile nitro-PAH. The chemical ionization technique is more gentle than electron impact and enhances sensitivity for detection of a molecular ion by decreasing the

amount of fragmentation. The NCI GC/MS method is especially sensitive and selective for the detection of nitro-PAH. This is due to the electro-negative nature of the nitro substitution which is highly susceptible to attachment of a thermal electron from the reagent gas plasma. Therefore, the NCI GC/MS method was used for the selected samples to determine nitro-PAH.

e. QA/QC for GC/MS Analysis

For each set of samples generated at the field test site, there was one field blank filter and XAD-2 trap, as well as one laboratory blank. These samples were analyzed concurrently with the field samples to determine whether there were significant sources of contamination to the samples. In addition, the field blank XAD-2 and filter and the laboratory method blank were spiked with the four perdeuterated PAH recovery standards to demonstrate PAH recovery in the absence of the matrix. The field blank XAD-2 was spiked by the sampling team with the d₁₂-benzo[e]pyrene and d₁₂-benzo[k]fluoranthene immediately after sampling. The methylene chloride extraction solvent was spiked in the laboratory with the d₁₂-chrysene and d₁₂-benzo[a]pyrene before the XAD-2 was extracted.

In the quantitative GC/MS analysis, the sample extracts or fractions were spiked with the internal standard, 9-phenylanthracene, immediately prior to GC/MS analysis. This PAH does not occur naturally, and thus does not pose a problem as an interferent. The use of an internal standard from the same compound class as the compounds to be quantified and having an average molecular weight and elution time of those compounds to be quantified enhances the analytical precision of the quantification. This is because an average correction factor for injection technique, chromatographic active site effects and slight variations in the daily mass spectrometer tuning is applied to the quantification of all compounds.

The ordering of samples and standards for GC/MS analyses ensures that standard analyses bracket all of the sample analyses. In general, one set of standards over the calibration range are analyzed first to ensure linearity and range.

A three-point standard curve is generated for each of the target compounds. These standards are analyzed in triplicate along with a blank sample which tests the baseline. For each standard, 2 μ L are injected and the response compared to that of the internal standard. The computer determines a calibration factor for each of the target compounds which minimizes the difference in ionization efficiencies between the target compounds and the internal standard. The computer performs a least-squares analysis and provides a correlation coefficient and intercept. The correlation coefficient must be at least 0.990 for an acceptable calibration curve. After the calibration curve is established, the order of analysis is: standard, sample, sample, sample, standard until all analyses in a set have been completed. In this way, the calibration curve generated from the standard analyses accurately reflects the condition and operation of the mass spectrometer throughout a set of samples.

The validity of the calibration curve is monitored by analyzing successive calibration solutions using the curves and comparing the measured value obtained with the known value. Quantification within 20 percent of the true value is considered acceptable and requires no reanalysis of the sample.

Mass spectral intensities for the calibration compound FC-43 are also recorded daily and these intensities are used to verify that the ion balance tuning of the mass spectrometer has not varied significantly during the analysis of the sample extracts.

f. Spiked Samples and Blanks

Selected XAD-2 traps and filter samples were spiked as soon as possible after sampling with known amounts (0.5 μ g) of d₁₂-benzo[e]-pyrene and d₁₂-benzo[k]fluoranthene. They were also spiked with known amounts (0.5 μ g) of d₁₂-benzo[a]pyrene and d₁₂-chrysene in the laboratory immediately before extraction. Analysis of these spiked samples permits assessment of PAH losses in sample handling and in sample preparation. Samples to be used for bioassay cannot be spiked with active compounds. The information is not used to adjust analysis data for loss but rather to estimate a range for data validity.

Analysis of at least one blank for each sample type was performed. Filter and XAD-2 blanks were subjected to the same field conditions as the materials used for actual sample collection. All reagents were added to the blank samples in the same quantity and from the same lot as those used for the actual samples. The blank samples were analyzed concurrently with the actual samples using the same preparation and analysis procedures for both blanks and samples.

SECTION III

RESULTS

A. AEROSOL MASS CONCENTRATION

The exhaust aerosol mass collected on the 47-mm Millipore® filters and on the 20 by 25 cm quartz fiber high-volume filters are presented in Table 3. Also indicated in this table are the exhaust volume sampled by each filter and the exhaust aerosol concentration. The final row of the table indicates the average change in the apparent mass of several blank filters of each type. These blank filters were not used for sampling, but were tare weighed, and stored and shipped in the same fashion as the sample filters. For the calculation of the exhaust aerosol mass concentration, any weight change of a sample filter which was less than one standard deviation above the average blank weight change was considered to be below our detection limit. The average weight gain of the blanks was then subtracted from the sample filters' net weights, and this difference was divided by the sample volume to arrive at the aerosol mass concentration in the engine exhaust.

B. AEROSOL COMPOSITION

Results of the SSMS analyses of the Millipore® filters are presented in Table 4. With the exception of carbon, nitrogen, and oxygen, all elements from lithium to uranium are detected by this technique. Those elements not listed in the table were not present above detection limits, which are from 1 to 10 ng/m³, depending on the element.

Clearly, one expects that the emitted particles found in jet engine exhaust will be principally carbonaceous particles. The results presented below indicate the amounts of target PAH and NO₂-PAH compounds which are associated with the particles. These are but a few of the compounds which can be adsorbed by the particles. Table 5 presents the total extractable organic mass found associated with the particles collected on the quartz fiber filter media.

TABLE 3. FILTER MASS COLLECTIONS AND APPARENT
EXHAUST AEROSOL MASS CONCENTRATIONS

	MILLIPORE® FILTER			HIGH-VOLUME FILTER		
	NET, mg	VOLUME, m ³	CONCENTRATION, mg/m ³	NET, mg	VOLUME, m ³	CONCENTRATION, mg/m ³
F101 Idle	0.512	1.03	0.25	15.32	36.2	0.35
44%	0.458	1.04	0.20	-7.35	34.8	ND
75%	0.252	1.01	ND ^(a)	6.71	34.6	0.12
100%	0.280	1.01	ND	7.60	34.0	0.15
F110 Idle	0.558	0.95	0.32	5.81	35.4	0.09
30%	0.281	1.07	ND	-1.65	35.1	ND
63%	0.471	1.01	0.21	-4.02	34.8	ND
100%	0.601	1.04	0.33	-1.59	33.1	ND
Blanks ^(b)	0.255 ± 0.053		--	2.63 ± 2.86		--

(a) Filter net mass is below detection limit.

(b) Net weight gains for blank values are means of seven Millipore® filters and of five quartz fiber high-volume filters, with the indicated standard deviations.

TABLE 4. ELEMENTAL CONCENTRATIONS IN EXHAUST AEROSOL ($\mu\text{g}/\text{m}^3$)

	F110				F101				BLANK
	IDLE	30%	63%	100%	IDLE	44%	75%	100%	
B	0.3	0.05	0.05	0.5	0.15	0.05	0.07	0.07	0.15
Na	10	5	3	5	5	2	3	5	10
Mg	3	0.6	0.30	10	0.3	0.3	2	5	5
Al	1	0.3	0.7	1	0.7	0.7	0.7	1.5	0.3
Si	40	40	10	40	40	7	15	20	20
P	0.5	0.1	0.1	0.15	0.3	0.15	0.15	0.3	0.5
S	7	4	4	10	7	4	4	1.5	4
Cl	0.5	0.2	0.1	0.5	0.2	0.1	0.05	0.05	1
K	2	0.7	0.5	0.7	0.7	1	0.7	0.7	2
Ca	40	7	4	30	15	7	4	7	15
Ti	0.07	0.005	0.02	0.7	0.05	0.05	0.05	0.07	0.1
V	0.006	0.0003	0.0015	0.015	0.0015	<0.0006	0.0006	0.0015	0.0015
Cr	0.02	0.03	0.03	0.7	0.1	0.06	0.06	0.3	0.2
Mn	0.03	0.015	0.02	0.07	0.02	0.015	0.015	0.010	0.02
Fe	1	0.3	0.3	3	0.3	0.3	0.3	0.15	0.3
Co	<0.003	<0.003	0.015	0.15	<0.003	<0.003	<0.003	0.15	<0.003
Ni	0.02	0.002	0.05	0.5	0.002	0.01	0.02	0.5	<0.0015
Cu	1	0.4	0.4	0.7	0.7	0.4	0.7	0.4	2
Zn	0.2	0.05	0.6	2	1	0.2	0.2	0.15	0.5

TABLE 4. ELEMENTAL CONCENTRATIONS IN EXHAUST AEROSOL ($\mu\text{g}/\text{m}^3$) (CONCLUDED)

	F110				F101				BLANK
	IDLE	30%	63%	100%	IDLE	44%	75%	100%	
Sr	0.02	0.002	0.003	0.2	0.007	0.007	0.007	0.004	0.02
Zr	0.004	<0.003	0.003	0.004	0.01	<0.005	0.004	0.003	0.7
Ba	0.15	0.003	0.07	5	0.15	0.15	0.05	0.02	0.04
Pb	0.015	<0.005	0.005	0.04	0.05	<0.005	0.01	0.05	0.015

TABLE 5. PARTICULATE EXTRACTABLE ORGANIC
MASS CONCENTRATION ($\mu\text{g}/\text{m}^3$)

ENGINE	POWER LEVEL	EXTRACTABLE ORGANIC MASS
F110	Idle	79
F110	30%	54
F110	63%	52
F110	100%	48
F101	Idle	140
F101	44%	72
F101	75%	75
F101	100%	140
Ambient	--	38

C. PAH AND NO₂-PAH CONCENTRATIONS

Tables 6 through 9 contain the measured concentrations of the target PAH and NO₂-PAH compounds. These data are separated by engine, with vapor phase (XAD) and particulate (Filter) portions of each compound listed in adjacent columns. Table 10 contains the total extractable organic mass collected on the XAD sorbent.

D. EXHAUST PARAMETERS

The exhaust gas temperature was measured using thermocouples positioned at the face of the high-volume filter and at the exit from the XAD cartridge. In all cases, these temperatures agreed, and the value is listed in Table 11 under the heading of Exhaust Temperature. The exhaust gas velocity pressure was measured during each sampling operation and used as a basis for calculating the gas flow rate through the exhaust stack. This mass flow rate was multiplied by the number of individual stacks (56) to estimate the total flow of gas through the engine test cell. This is only a rough approximation of the total flow rate, but it was not within the scope of this project to perform a full characterization of the exhaust stack flow patterns. Also indicated in Table 11 are the engine air flow rates measured by the test cell operators.

TABLE 6. TARGET PAH CONCENTRATIONS IN THE VAPOR-PHASE (XAD) AND PARTICULATE (FILTER) PORTIONS OF F110 EXHAUST AT VARIOUS POWER SETTINGS (ng/m³)

COMPOUND	IDLE		30% POWER		63% POWER		100% POWER	
	XAD	FILTER	XAD	FILTER	XAD	FILTER	XAD	FILTER
Naphthalene	1200	1.8	420	2.3	500	1.8	290	1.7
1-Methylnaphthalene	1900	2.4	590	2.7	640	2.1	380	2.0
2-Methylnaphthalene	1100	1.2	360	1.6	400	1.2	200	1.1
1,2-Dimethylnaphthalene	610	0.84	200	1.0	220	1.0	140	1.0
Dimethylnaphthalene	1000	1.6	360	1.8	400	1.6	240	1.9
1,4,8,2,3-Dimethylnaphthalene	280	0.73	100	0.58	110	0.80	71	0.73
2,6-Dimethylnaphthalene	97	0.27	33	0.18	33	0.29	23	0.27
Acenaphthylene	30	0.51	12	0.29	20	0.20	7.4	0.45
Acenaphthene	55	0.81	30	1.2	41	1.0	33	0.97
Dibenzothiophene	20	1.4	12	1.0	16	1.0	9.0	1.3
Phenanthrene	230	11.0	130	10	220	11	240	13.0
Anthracene	12	1.1	5.1	0.84	8.5	0.80	11	0.78
Fluoranthene	46	4.8	25	4.5	46	4.9	150	5.8
Pyrene	35	2.5	15	3.3	25	2.6	400	2.8
Cyclopenta[c,d]pyrene	ND(a)	0.53	ND(a)	0.65	ND(a)	0.69	ND(a)	0.30
Benz[a]anthracene	2.6	0.53	1.1	0.83	1.6	0.24	3.1	0.15
Chrysene	5.2	0.96	2.1	1.1	3.8	0.55	5.3	0.58
Benzofluoranthenes	ND	1.1	ND	1.4	ND	0.40	ND	0.26
Benzo[e]pyrene	ND	0.57	ND	0.71	ND	ND(a)	ND	0.15
Benzo[a]pyrene	ND	0.61	ND	0.70	ND	ND	ND	0.20
Indeno[1,2,3-c,d]pyrene	ND	0.62	ND	0.52	ND	ND	ND	0.11
Dibenzo[a,h]anthracene	ND	0.70	ND	0.40	ND	ND	ND	0.066
Benzo[g,h,i]perylene	ND	0.65	ND	0.52	ND	ND	ND	0.14

(a)ND = Not detected.

TABLE 7. TARGET PAH CONCENTRATIONS IN THE VAPOR-PHASE (XAD) AND PARTICULATE (FILTER) PORTIONS OF F101 EXHAUST AT VARIOUS POWER SETTINGS (ng/m³)

COMPOUND	IDLE		44% POWER		75% POWER		100% POWER	
	XAD	FILTER	XAD	FILTER	XAD	FILTER	XAD	FILTER
Naphthalene	680	0.73	190	1.2	300	1.1	240	1.7
1-Methylnaphthalene	660	0.63	240	1.5	320	1.6	240	2.9
2-Methylnaphthalene	410	0.35	140	0.84	180	0.96	150	1.4
1,2-Dimethylnaphthalene	180	0.49	88	0.69	120	0.75	100	0.15
Dimethylnaphthalene	340	0.11	170	1.4	210	1.3	190	2.6
1,4,8,2,3-Dimethylnaphthalene	100	0.11	53	0.90	84	0.75	64	1.1
2,6-Dimethylnaphthalene	32	0.43	12	0.27	14	0.35	18	0.53
Acenaphthylene	14	0.13	4.8	0.52	9.8	0.20	8.2	0.22
Acenaphthene	29	0.59	35	1.0	45	0.58	48	0.79
Dibenzothiophene	20	0.82	12	0.95	11	1.4	11	0.21
Phenanthrene	130	6.1	140	9.0	280	20	320	36
Anthracene	11	0.78	6.7	0.89	18	1.0	15	0.84
Fluoranthene	27	3.7	31	4.9	46	7.3	97	7.4
Pyrene	18	2.7	22	3.1	46	4.6	60	2.8
Cyclopenta[c,d]pyrene	ND(a)	0.84	ND(a)	0.50	ND(a)	0.49	2.3	0.56
Benz[a]anthracene	2.2	0.33	3.0	0.27	2.3	0.17	5.4	0.21
Chrysene	3.6	0.34	4.2	0.68	4.5	0.64	7.9	0.61
Benzo[a]fluoranthene	ND	0.38	ND	0.37	ND	0.24	ND(a)	0.17
Benzo[e]pyrene	ND	0.11	ND	ND(a)	ND	ND(a)	ND	ND(a)
Benzo[a]pyrene	ND	0.19	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	ND	0.15	ND	0.25	ND	ND	ND	ND
Dibenzof[a,h]anthracene	ND	0.16	ND	0.30	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND	0.20	ND	0.29	ND	ND	ND	ND

(a)ND = Not detected.

TABLE 8. F110, NO₂-PAH COMPOUND CONCENTRATION (ng/m³)

COMPOUND	IDLE		30% POWER		63% POWER		100% POWER	
	XAD	FILTER	XAD	FILTER	XAD	FILTER	XAD	FILTER
2-Nitro-1-naphthol	12	0.32	11	0.19	15	0.12	14	0.13
4-Hydroxy-3-nitrobiphenyl	0.55	0.071	0.18	0.061	0.59	0.072	0.69	0.059
1-Nitronaphthalene	1.6	0.055	0.59	0.17	0.75	0.067	1.1	0.039
2-Nitronaphthalene	0.55	0.039	0.26	0.029	0.33	0.037	0.53	0.022
9-Nitroanthracene	0.75	0.082	1.1	0.075	1.5	0.064	17	0.052
9-Nitrophenanthrene	0.20	0.045	0.095	0.045	0.11	0.064	1.2	0.12
Nitroanthracene/phenanthrene isomer	0.18	0.024	0.083	0.032	0.34	0.027	18	0.013
3-Nitrofluoranthene	ND	0.032	ND	0.025	ND	0.049	ND	0.021
1-Nitropyrene	ND	0.087	ND	0.22	ND	0.19	0.50	0.16
6-Nitrochrysene	ND	ND	ND	ND	ND	ND	ND	ND
Dinitropyrene	ND	ND	ND	ND	ND	ND	ND	ND

ND = Not detected.

TABLE 9. F101, NO₂-PAH COMPOUND CONCENTRATION (ng/m³)

COMPOUND	IDLE		44% POWER		75% POWER		100% POWER	
	XAD	FILTER	XAD	FILTER	XAD	FILTER	XAD	FILTER
2-Nitro-1-naphthol	18	0.095	7.5	0.17	8.9	0.23	16	0.13
4-Hydroxy-3-nitrobiphenyl	0.52	0.037	0.28	0.072	0.77	0.057	1.6	0.039
1-Nitronaphthalene	2.9	0.049	0.39	0.051	0.40	0.075	1.0	0.093
2-Nitronaphthalene	0.54	0.024	0.18	0.022	0.20	0.035	0.40	0.033
9-Nitroanthracene	0.62	0.035	0.50	0.053	2.8	0.069	5.3	0.046
9-Nitrophenanthrene	0.28	0.030	0.11	0.012	0.083	0.037	0.35	0.026
5 Nitroanthracene/phenanthrene isomer	0.14	0.012	0.10	0.010	1.9	0.014	5.3	0.013
3-Nitrofluoranthene	ND	0.017	ND	0.021	ND	0.028	ND	0.014
1-Nitropyrene	ND	ND	ND	0.15	ND	0.10	ND	0.10
6-Nitrochrysene	ND	ND	ND	ND	ND	ND	ND	ND
Dinitropyrene	ND	ND	ND	ND	ND	ND	ND	ND

ND = Not detected.

TABLE 10. VAPOR-PHASE EXTRACTABLE ORGANIC MASS
CONCENTRATIONS ($\mu\text{g}/\text{m}^3$)

ENGINE	POWER LEVEL	EXTRACTABLE ORGANIC MASS
F110	Idle	420
F110	30%	220
F110	63%	400
F110	100%	1900
F101	Idle	230
F101	44%	380
F101	75%	320
F101	100%	400
Ambient	--	80

TABLE 11. EXHAUST GAS TEMPERATURE AND FLOW RATES

ENGINE	POWER LEVEL	TEMP, °C	STACK EXHAUST FLOW kg/s	ENGINE AIR FLOW, kg/s
F110	Idle	63	68	40
F110	30%	59	350	60
F110	63%	74	520	89
F110	100%	100	690	120
F101	Idle	51	170	57
F101	44%	64	450	110
F101	75%	81	610	140
F101	100%	93	700	160

SECTION IV

DISCUSSION

A. AEROSOL MASS CONCENTRATION

Previously reported measurements of particulate mass concentrations in jet engine exhaust indicate that a value on the order of tens of mg/m^3 is typical, with considerable variation between engine types, and between engines, depending upon the time logged since major overhaul.

Measurements performed on two TF30-P414 engines--one newly rebuilt and one with many hours of use--indicated that, at military power, the newly rebuilt engine's exhaust contained 9 to 15 mg/m^3 particulate matter, while the heavily used engine's exhaust contained 63 to 86 mg/m^3 (Reference 4). That range of values is in good agreement with measurements reported for newly rebuilt TF30-P103 and TF30-P109 engines (Reference 5). This latter reference also presents data for the J79-17G (smokeless) engine showing less than 5 mg/m^3 at full power, the TF41-A2 at nearly 50 mg/m^3 , and TF33-P3 and TF33-P7 engines approximately midway between those values. Those results were based on samples collected at the engine exhaust plane, but other investigators have found no significant differences between the particulate mass concentration or particle size distribution measured at the exhaust plane and those measured at the test cell exhaust stack (References 6,7).

In the absence of available information regarding the exhaust particulate mass concentration to be expected for the F101 and F110 engines, the sampling and gravimetric analysis procedures were designed to enable measurement of concentrations as low as 1 mg/m^3 . Blank filters were tared and gross weighed to provide an indication of the mass change of the filter media which would be attributable to storage conditions, shipment, and random fluctuations within the bounds established for the weighing laboratory and balance. As indicated in Table 3, both sets of filter blanks exhibited an increase in mass, which was accounted for in completing the net mass gain for the sample filters. The magnitude of the mass change relative to the tare weights of the blanks is roughly 0.3 percent for the Millipore® media and 0.07 percent for the quartz fiber

media. The variability is much greater for the quartz fiber media. One would expect this because this media is much more prone to variable losses of fibers than the Millipore® cellulose acetate material is. This is also indicated by the negative weight changes found in half of the sample filters.

The exhaust plane aerosol samples collected in the comparison project (Reference 1) indicated mass concentrations less than 0.4 mg/m^3 in all cases except for the F101 at idle, which was less than 1 mg/m^3 . The results presented in Table 3 confirm that the exhaust aerosol mass concentration is less than 0.4 mg/m^3 in all cases for these engines. At these extremely low concentrations, it is not reasonable to attempt to extract more detailed information from the measurements obtained. The aerosol mass emissions of these two engines are clearly lower than those of any of the engines listed in the above discussion.

B. AEROSOL COMPOSITION

In examining the SSMS results presented in Table 4, one must keep in mind that this technique is not especially precise, although it has great sensitivity. The only elements of potential interest in that table are those which are generally present in the samples at a higher concentration than was found in the blank filter media. The crustal elements Al and Si appear to be enriched in the samples, relative to the blank, and these merely indicate the presence of a small amount of wind-blown soil in the sample.

Iron is indicated in a few of the samples. The elements Ni and Co, however, are present at levels well in excess of the blank, especially at higher engine power levels. This may be indicative of greater wear of turbine components fabricated from alloys containing cobalt and nickel.

Inspection of Table 4 reveals that there are not significant emissions of heavy metals by these engines, and that the exhaust aerosol mass accounted for by inorganic components is only a small portion of the total.

The total extractable organic mass concentrations presented in Table 5 indicate that this material may account for up to one-third of the total aerosol mass. Because of the very small masses of particulate matter

collected, however, a more precise accounting of the extractable and carbonaceous aerosol mass cannot be made.

C. PAH AND NO₂-PAH CONCENTRATIONS

Tables 6 through 9 contain the measured concentrations of all target PAH and NO₂-PAH compounds measured in the engine exhaust samples. Examination of these data reveals several trends which may be duplicated in other turbine engines' exhaust.

The phase distribution of the PAH compounds is, perhaps, the most obvious feature of these data. The compounds ranging from naphthalene through the four-ring compounds, fluoranthene and pyrene are principally (>90 percent, typically) found in the vapor phase under the sampling conditions of this study. The higher than ambient temperatures at which the exhaust samples were necessarily collected do not appear to have resulted in a large distortion of the phase distribution. The phase distribution of the four-ring PAH shift slightly from particulate to vapor phase as the engine power level (hence exhaust temperature) increases. The extent of this shift is not large, however. For the F101 engine, the shift is from about 14 percent of the four-ring compounds being in the particulate phase at idle, to about 6 percent at full power. For the F110, the corresponding shift is from about 8 percent to about 3 percent.

For the five-ring compound, cyclopenta[c,d]pyrene, there is only one instance of this material being detected in the vapor-phase sample. For benzofluoranthene and beyond, these PAH are found exclusively associated with the particles collected from the exhaust.

The same trends apply to the NO₂-PAH phase distribution, but only 3-nitrofluoranthene and 1-nitropyrene are present at high enough concentrations to be detected in the aerosol samples.

There is, in general, a dependence of the PAH concentrations on the engine and engine power level. The F110 exhaust concentrations of these PAH are approximately twice those for the F101 exhaust. Performing a simple linear regression on the PAH concentrations in Tables 6 and 7 for the compounds naphthalene through pyrene provides a coefficient of determination, $r^2 = 0.92$, with the F110 concentrations being 2.4 times the

F101 values. This indicates that there is not a large difference in the relative proportions of these exhaust components.

Within the data obtained for each engine there is a general trend towards decreasing PAH concentrations with increasing engine power level. A linear regression of the PAH concentrations for naphthalene through dibenzothiophene yields the following relations:

- F110: $C(100\%) = 11.8 \text{ ng/m}^3 + 0.203 C(\text{idle})$ $r^2 = 0.98$
- F101: $C(100\%) = 22.9 \text{ ng/m}^3 + 0.341 C(\text{idle})$ $r^2 = 0.94$

where $C(X)$ denotes the PAH concentration (ng/m^3) for the power level, X . The high values of the coefficient of determination are a strong indication that there are no important changes in the relative concentrations of these compounds as the engine power changes. Rather, the entire set of compounds increases or decreases together. This can also be seen in Figures 3 and 4. These figures also show that there is not much difference between the exhaust concentrations of these compounds measured at the two intermediate power levels. These concentrations range from 0.3 to approximately 0.4 of the idle exhaust levels.

The concentrations of the three-ring and larger PAH compounds (phenanthrene and below, in Tables 6 and 7) do not demonstrate a clear dependence on engine power level. For the F101 engine, the phenanthrene concentrations increase with engine power level. For the F110, however, the idle and full power exhaust concentrations are nearly identical. These patterns are also followed by chrysene, benz[a]anthracene, and cyclopenta[c,d]pyrene. Those PAH compounds found only in the particulate samples, i.e., benzo[fluoranthene]s through benzo[g,h,i]perylene in the tables, clearly decrease at the full power setting for both engines.

The data obtained in the companion project (Reference 1) indicate decreasing concentrations of all PAH with increasing power levels, with few exceptions. The discrepancy between those results and the exhaust cell stack measurements of phenanthrene, anthracene, fluoranthene, and pyrene is not understood at this time. In general, the correspondence between the PAH measurements made on the samples collected at the engine exhaust plane and at the test cell stack is quite good. At the idle power

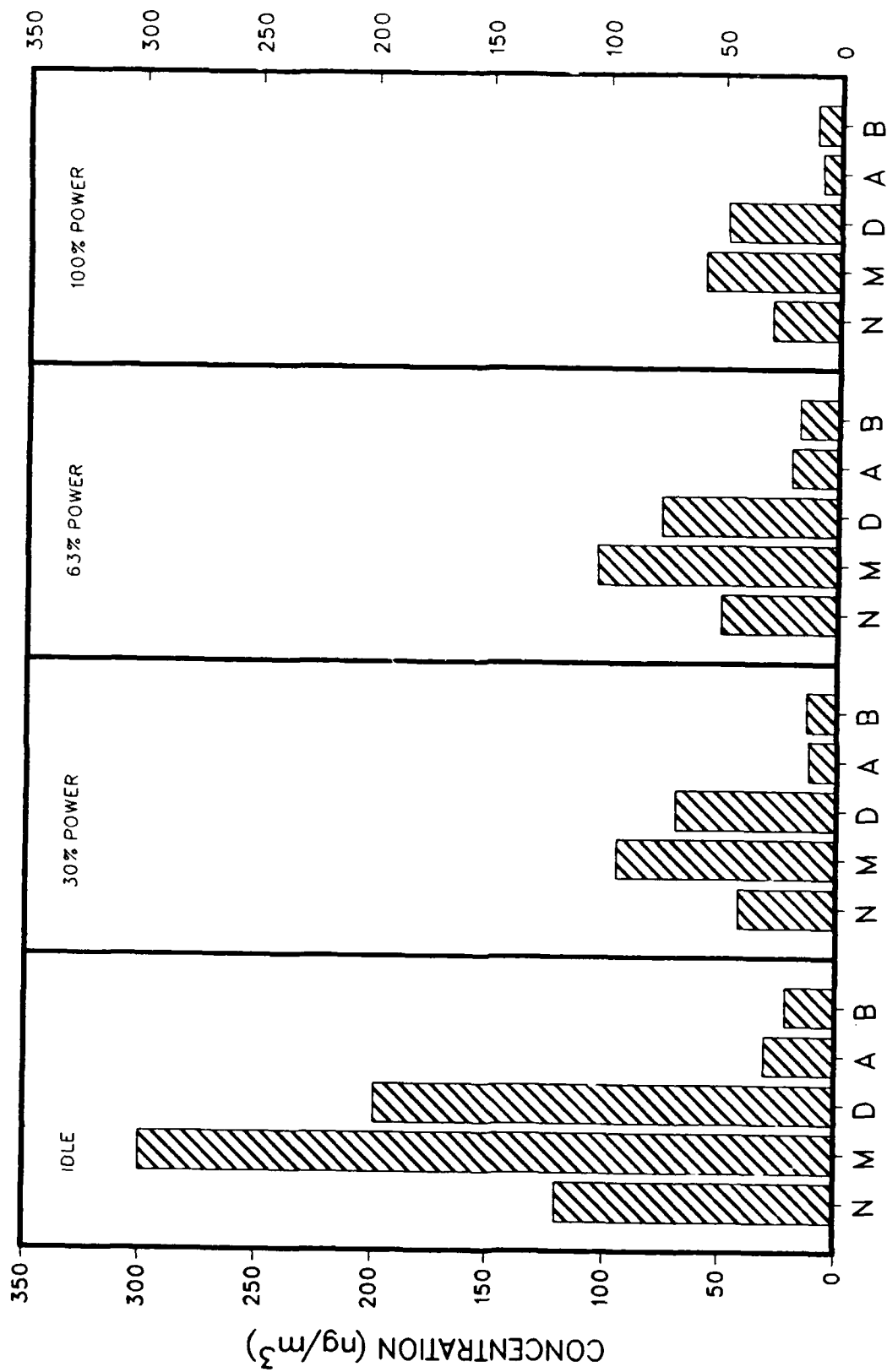


Figure 3. Concentrations of Several Target PAH Compounds in the F110 Exhaust at Indicated Power Levels. Concentrations of N, M, and D Have Been Divided by 10. (N = Naphthalene, M = 1- and 2-Methylnaphthalene, D = C₂-alkylnaphthalene isomers, A = Acenaphthalene, and B = Dibenzo-thiophene)

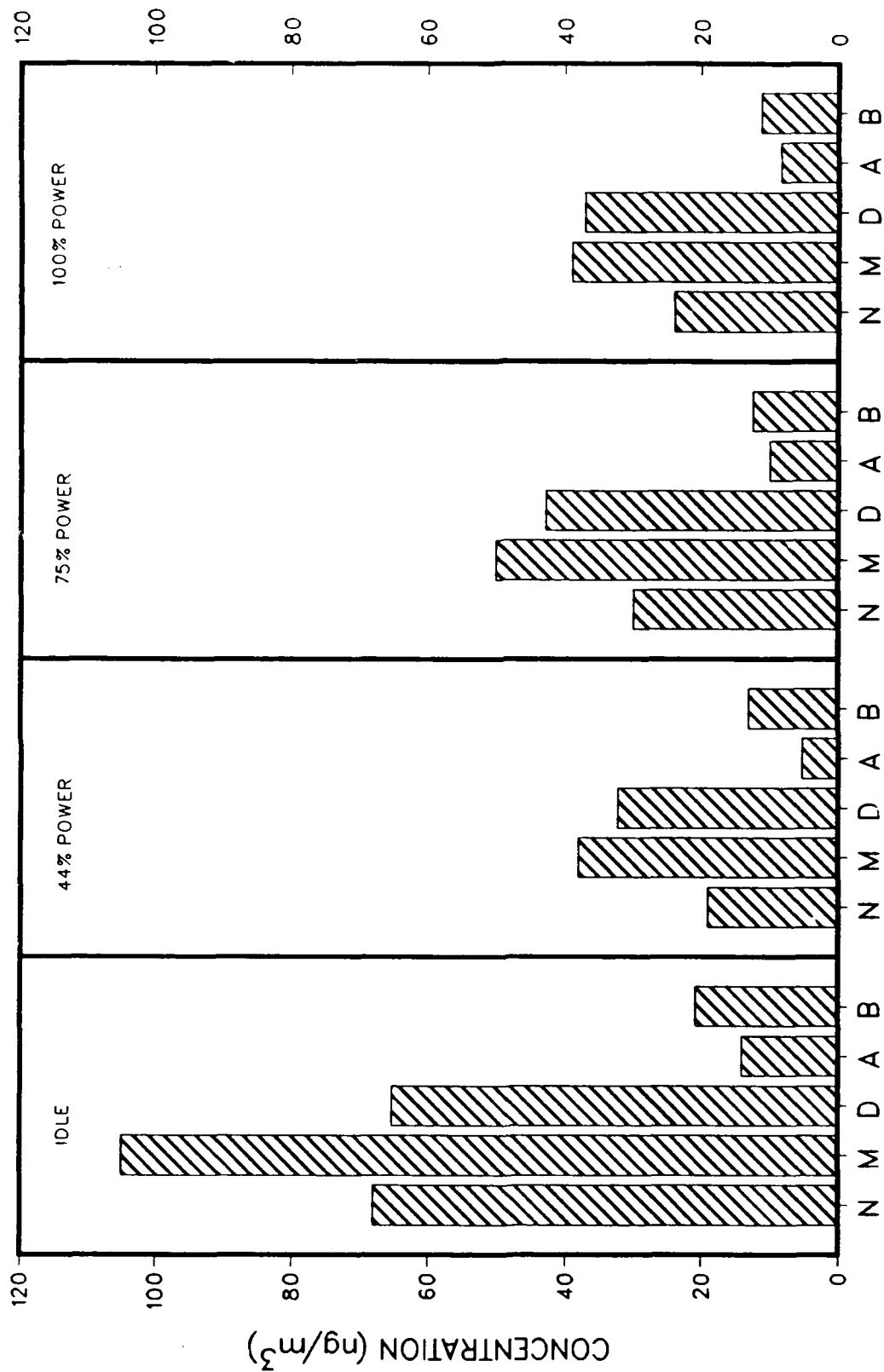


Figure 4. Concentrations of Several Target PAH Compounds in the F101 Exhaust at Indicated Power Levels. Concentrations of N, M, and D Have Been Divided by 10. (N = Naphthalene, M = 1- and 2-Methylnaphthalene, D = C2-alkyl-naphthalene Isomers, A = Acenaphthalene, and B = Dibenzothiophene)

level, for example, a linear regression of the PAH measurements results in the relations:

- F110: $C(\text{stack}) = -32.8 \text{ ng/m}^3 + 0.226 C(\text{exhaust plane})$
 $r^2 = 0.84$
- F101: $C(\text{stack}) = -15.5 \text{ ng/m}^3 + 0.266 C(\text{exhaust plane})$
 $r^2 = 0.97$.

where $C(X)$ denotes the PAH concentration (ng/m^3) measured at sampling location X . The high degree of correlation indicates no significant changes in the relative proportions of the PAH concentrations between the two sampling locations. The measured concentrations are presented in Figures 5 and 6, where each point corresponds to one PAH compound, and its coordinates represent the values measured at the two sampling locations. It is apparent in these figures that for the compounds whose concentrations are relatively low, the correlation between the data sets may not be so high as is indicated for the overall data.

For both engines, the exhaust plane PAH concentrations are approximately four times greater than the test cell stack concentrations. Unfortunately, the aerosol mass concentration measurements are too low to permit a meaningful comparison of values from the two sampling locations. The cause of the apparent discrepancy would appear to lie in the presence of diluting (noncombustion) air in the stack gas flow. Table 11 shows measured values of the engine air flow, and air flow rate estimates made on the basis of measurements performed at the top of the stack. The average value of the ratio of these flow rates is 4.3, meaning that the engine air flow is diluted by a factor of approximately four in its transit to the stack exit. Because the engine exhaust plane measurements were performed within the core of the engine exhaust plume, it is reasonable that these values should indicate concentrations approximately four times the diluted values measured at the top of the stack.

One final point should be raised regarding the PAH and NO_2 -PAH measurements performed. Examination of Table 10 indicates that the sum of the target PAH compounds quantified is only a very small portion of the total extractable organic mass found in the vapor samples of the engine exhaust. For the identification and quantification of the more prevalent

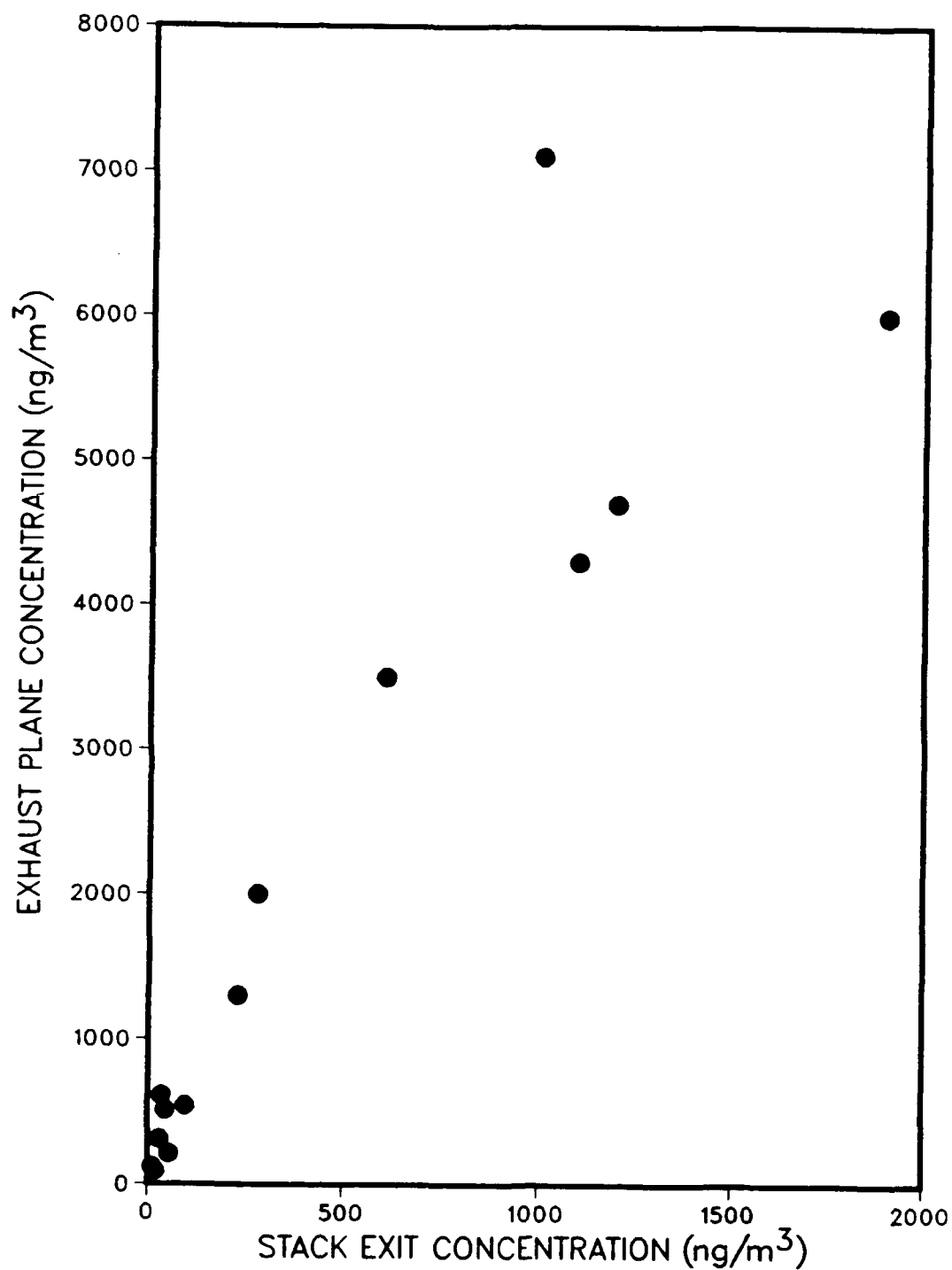


Figure 5. Concentrations of PAH Compounds Measured in F110 Exhaust Samples Collected at Idle from the Engine Exhaust Plane, and at the Test Cell Stack Exit. (Each Datum Denotes One Compound in Table 6.)

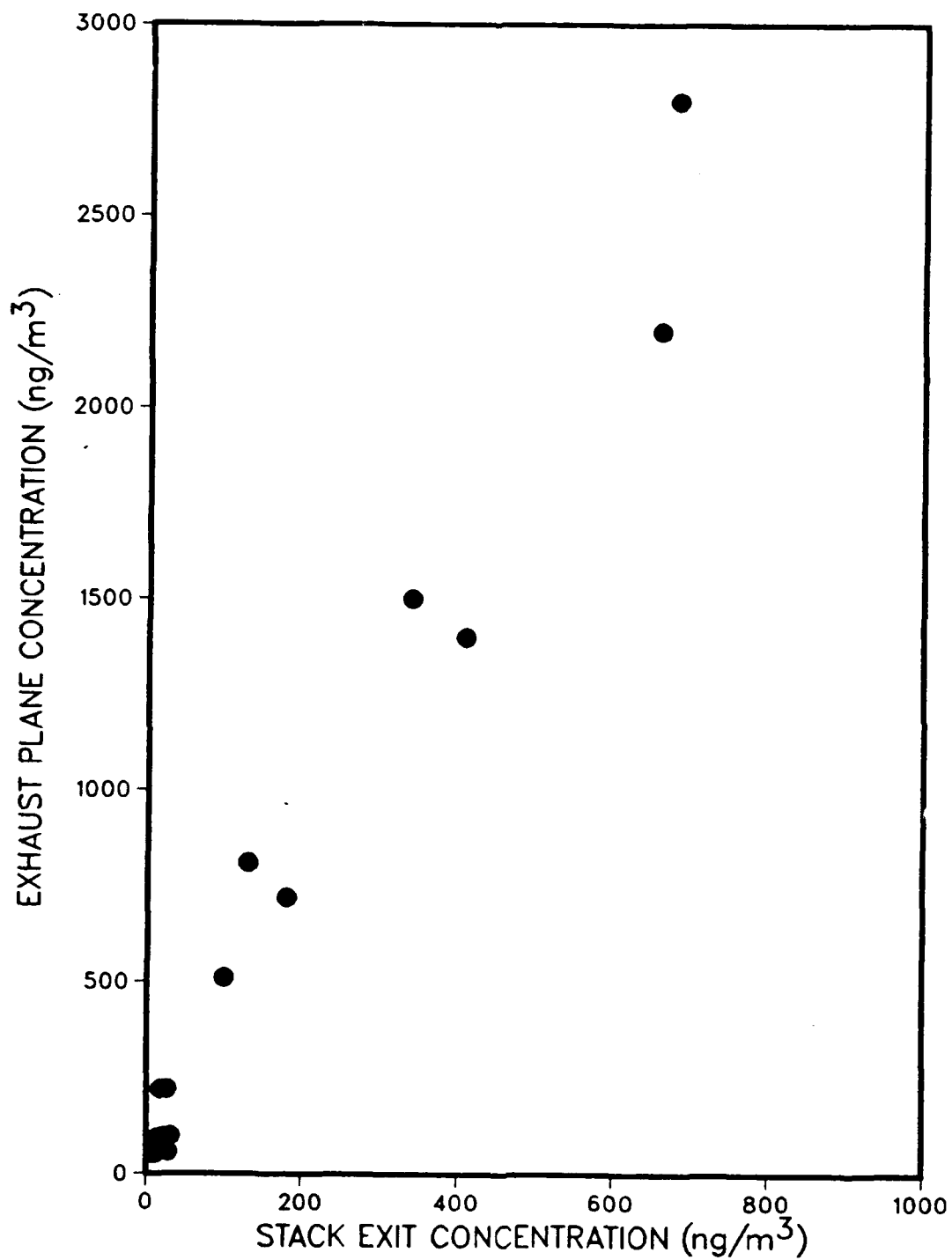


Figure 6. Concentrations of PAH Compounds Measured in F101 Exhaust Samples Collected at Idle from the Engine Exhaust Plane, and at the Test Cell Stack Exit. (Each Datum Denotes One Compound in Table 7.)

compounds found in the extractable organics, the reader is referred to the report covering the companion study (Reference 1).

D. PARTICLE MORPHOLOGY

The engine exhaust samples collected on Nuclepore® filters were analyzed using an ISI-DS13 Scanning Electron Microscope (SEM). The samples were not subjected to quantitative analyses, but the qualitative differences exhibited at different power levels merit discussions.

Previous work had indicated that the idle power level yielded the lowest concentration of particles in the engine exhaust. This is in qualitative agreement with the SEM analyses of these samples. Figure 7 depicts particles collected from the exhaust of the F101 engine operated at idle power. (Note that the pores in the filters are approximately 0.2 μm diameter.) The large (0.4 μm) spherical particles in this field are found only in the idle exhaust for these engines. Less visible in the micrograph are the more numerous small particles of diameter 0.05 μm . The particle distribution appears to be bimodal, but with a very low number concentration of the larger particles. A filter collected atop the stack in the absence of engine operation yielded collection of much fewer particles than any of the exhaust samples, and the particles which were present were small globular agglomerates.

At full (nonafterburning) power, the particle concentration in the engine exhaust was much higher, as shown in Figures 8 and 9. The particles are predominantly characterized as agglomerates composed of primary particles of diameter less than 0.1 μm . The "diameter" of the agglomerates rarely exceeds 0.2 μm . No significant differences are apparent in the exhaust particle samples for the two engines at any common power level. The presence of the agglomerates indicates formation of a high concentration of very fine particles near the engine's combustion zone. The high concentration of these particles, the high degree of turbulence in the gas flow near the engine exhaust plane, and the probable high charge on the combustion-generated particles contribute to a high rate of coagulation. As coagulation proceeds, the agglomerates seen in Figures 8 and 9 effectively scavenge a large fraction of the primary particles in the exhaust stream.

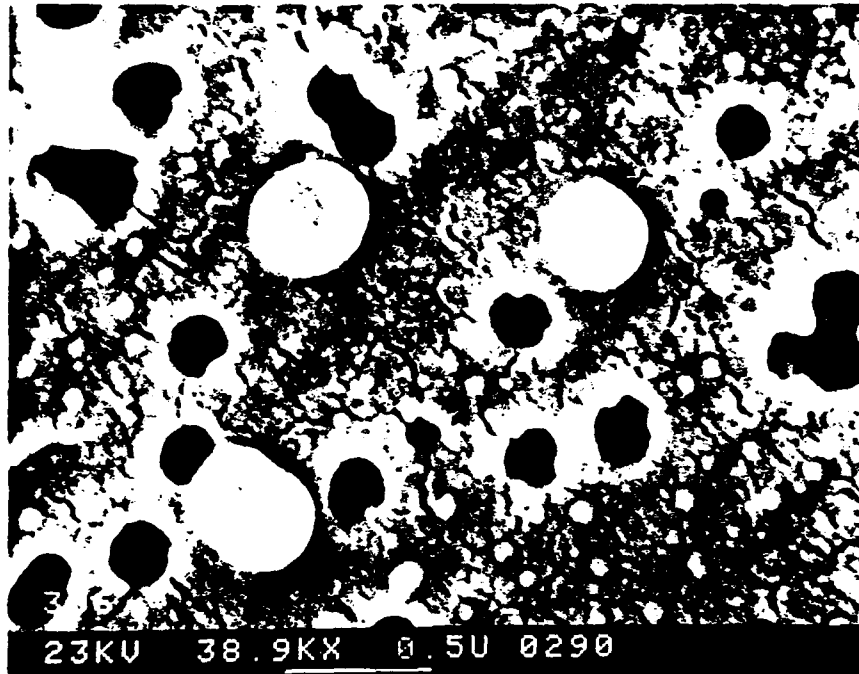


Figure 7. SEM Photomicrograph of Particles Collected from Exhaust of F101 Engine Operated at Idle Power

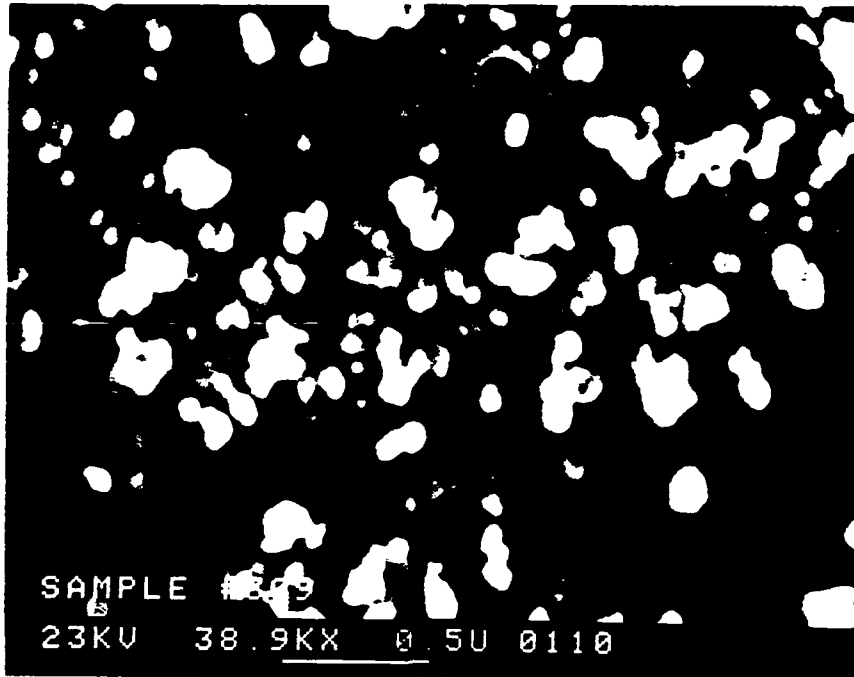


Figure 8. SEM Photomicrograph of Particles Collected from Exhaust of F101 Engine Operated at 100 Percent Power

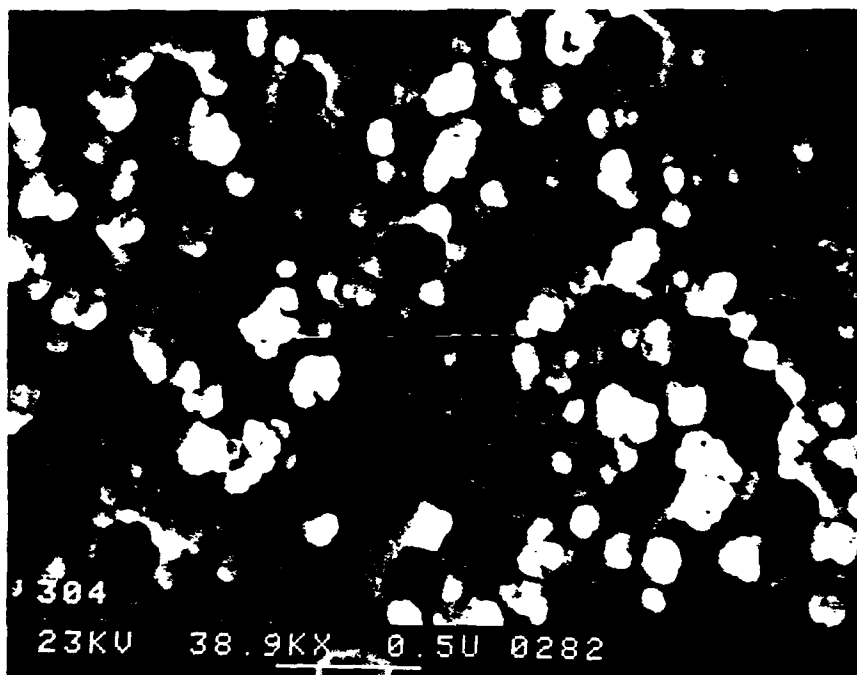


Figure 9. SEM Photomicrograph of Particles Collected from Exhaust of F110 Engine Operated at 100 Percent Power

SECTION V

CONCLUSIONS

This study has characterized several of the chemicals associated with the particles in the exhaust from the F101 and F110 engines at four operating power levels. The particles were collected from the exhaust gas and characterized with respect to inorganic elemental composition, total extractable organic mass, and target PAH and NO₂-PAH compounds.

An exhaust sampling system was designed and built for this task to enable collection of exhaust samples from the test cell stack exit. Samples were collected on XAD-2 resin (vapor phase components), quartz fiber filters, Millipore® and Nuclepore® filter media for the different analytical techniques employed.

Key conclusions drawn from the analyses follow:

- The aerosol mass concentration in the exhaust from these engines was very low, consistently less than 0.4 mg/m³ at the test cell stack. These measurements were performed with two different filter media, which produced similar results. These results were also confirmed by mass concentration measurements made in the companion study, using samples collected at the engine exhaust plane.
- Most of the target PAH compounds were found to decrease with increasing engine power level for both engines. The relative concentrations of the two- and three-ring PAH were very similar for the two engines and agreed reasonably well with measurements made on samples collected at the engine exhaust plane.
- As has been found in previous analyses of the organic constituents of gas turbine engine exhaust, the total contribution of PAH is but a very small portion of the total extractable organic mass, typically being on the order of 1 percent.
- The target PAH compounds are distributed between the vapor and particulate phase according to their molecular weight. The two- and three-ring compounds, which account for a very large portion (>90 percent) of the total PAH analyzed, are almost completely found in the

vapor phase, while the heaviest PAH compounds analyzed in this work are found exclusively associated with the particles.

- The particles collected at the test cell stack are principally small ($<0.2\ \mu\text{m}$) agglomerates of smaller ($<0.1\ \mu\text{m}$) primary particles for higher engine power levels. The indicated size is in rough agreement with measurements made on aerosol samples collected at the engine exhaust plane.

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